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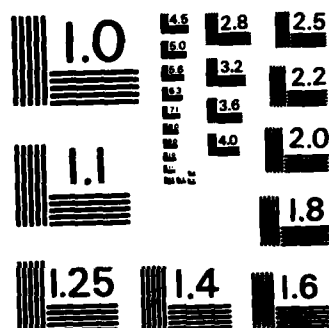
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Block Copolymers of Isotactic Polypropylene  
and 1,4 Polybutadiene

by

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September 24, 1985

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Two block copolymers of isotactic polypropylene and 1,4 polybutadiene were synthesized using techniques involving a transformation from anionic to Ziegler-Natta polymerization mechanisms. The yield of block copolymer was about fifteen percent (weight basis) in both polymerizations, the remainder being unreacted polybutadiene from the first block synthesis. Molecular characterization experiments and model reactions were consistent with a block-like structure for the copolymers; definitive evidence for the proposed		

molecular structure was obtained through transmission electron microscopy which clearly revealed microphase-separated morphologies characteristic of block copolymers.

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### Synopsis

Two block copolymers of isotactic polypropylene and 1,4 polybutadiene were synthesized using techniques involving a transformation from anionic to Ziegler-Natta polymerization mechanisms. The yield of block copolymer was about fifteen percent (weight basis) in both polymerizations, the remainder being unreacted polybutadiene from the first block synthesis. Molecular characterization experiments and model reactions were consistent with a block-like structure for the copolymers; definitive evidence for the proposed molecular structure was obtained through transmission electron microscopy which clearly revealed microphase-separated morphologies characteristic of block copolymers.

### Introduction

Block copolymers containing at least one moiety comprised of isotactic polypropylene have been discussed in numerous publications and various reviews (1,2). In most cases, sequential feeding of monomers to reactors containing Ziegler-Natta catalysts has been used in attempts to generate blocks of pure iPP attached to rubbery poly(ethylene-co-propylene) blocks. Owing to uncertainties in the mechanism of Z-N polymerization, particularly in terms of the lifetimes of growing chains in these systems, there is a considerable amount of ongoing disagreement about the true molecular structure of these sequential Z-N copolymers; there are groups which find significant evidence for block junctions in certain cases (3-5) while others find that the reaction products of the sequential copolymerizations are essentially identical to a mixture of unattached homopolymers (6). In most cases the claimed block copolymer structure has not been proven unequivocally, but instead has been inferred from physical properties data and the method of synthesis.

Synthetic routes other than sequential Z-N polymerization of propylene with other olefins have been used in attempts to prepare block copolymers containing polypropylene. Del Giudice and coworkers (7,8) used fractional crystallization to separate a block copolymer of isotactic polystyrene and iPP from the homopolymers obtained in a nonisothermal sequential Z-N polymerization. Doi and coworkers (9) used coupling of living polystyryllithium and an iodine terminated syndiotactic polypropylene to produce a diblock copolymer. A sequential Z-N/free radical scheme was proposed by Doi (10) in the synthesis of a diblock copolymer of syndiotactic polypropylene and syndiotactic polymethylmethacrylate.

While diblocks such as these are novel, finding a true diblock copolymer of iPP and a low-T<sub>g</sub> rubber remains a focus of interest owing to the potential of using such a diblock as a morphology control agent in rubber modified compositions of iPP. Such materials offer one possible route to imparting improved low-temperature properties, particularly impact resistance, to iPP.

With these ideas in mind, we set out to synthesize diblock copolymers of polybutadiene (predominantly 1,4 microstructure) and iPP using a reaction scheme employing a transformation from homogeneous anionic polymerization to a heterogeneous Ziegler-Natta reaction. Our choice of this synthetic route was guided by the recent work of Fontanille (11-13) and Richards (14,15) who, for different purposes, have been investigating transformations from anionic to Z-N mechanisms. The recent work of Wnek and coworkers (16,17) was also useful in planning our reaction scheme, preliminary details of which have appeared elsewhere (18).

## Experimental

### Materials

All synthetic work was performed under inert conditions using carefully purified and analyzed materials. Ultra-high-purity argon was purified still further using a deoxygenating BASF copper-based catalyst and Linde 4x molecular sieves. A double manifold system (Ace Glass) containing the purified argon and a vacuum line permits alternate evacuation and flushing of the reaction equipment.

Reagents were purified under vacuum conditions using a manifold which was equipped with Teflon /O-ring valves and which maintains  $10^{-4}$  torr vacuum. This system eliminates the use of vacuum grease, a condition which has proven advantageous in previous work (19). A monomer gas purification line was used in conjunction with the high vacuum manifold. It consists of a gas washing chamber containing 10% NaOH solution, a NaOH column, a 4x molecular sieves column, a large capacity oxygen trap and an indicating deoxygenating column. This system provides for deoxygenating, drying and collecting of monomer gases. The 1,3 butadiene passes through the purification line and is collected on calcium hydride at  $-78^{\circ}\text{C}$ , stirred for 24h, frozen, degassed and thawed. The liquid butadiene is then distilled through a series of flasks containing fresh sodium mirrors. The propylene gas passes through the purification line and directly into the reactor when required.

The reaction medium was n-hexane. It was fractionally distilled twice under inert conditions, the second time in the presence of living divinylbenzene gels (20). The middle fraction from the second distillation was recovered directly in the reactor under argon. The butyllithium initiator, nominally 1.6M in n-hexane, was titrated just prior to use by a method similar to that of Eppley and Dixon (21). Transfer to the reactor was accomplished through a self-sealing



neoprene septum using a flamed, argon purged, gas-tight syringe. Titanium tetrachloride was cryogenically distilled under high vacuum and degassed prior to use. It was also transferred to the reactor by syringe through the neoprene septum. When small quantities of  $\text{TiCl}_4$  were needed, a hexane solution was used to improve accuracy of transfer.

A key to the success of the polymerization reactions was the design of the reactor, which consisted of a 2000 ml flask modified with Ace Glass threaded Teflon /O-ring connectors. Prior to use the entire reactor assembly was heated to  $300^\circ\text{C}$  for 24 hrs while maintaining high vacuum. When cool, the reactor was filled with argon to a pressure of 900 torr.

#### Synthesis

Two successful syntheses of PB/iPP diblock copolymers were carried out as well as certain control reactions and homopolymerizations. For the diblock synthesis in each case the polybutadiene block was produced first using anionic polymerization reactions. In one case (COP 1) n-butyllithium was the initiator; for the other copolymerization (COP 2) sec-butyllithium was used. In both cases just prior to the reaction, purified frozen butadiene was sealed in a calibrated delivery burette which is part of the reactor assembly. The frozen butadiene was allowed to warm gradually and was then maintained at  $0^\circ\text{C}$  by a copper coil jacket which circulates water from an adjacent ice-salt bath. The mass of butadiene is calculated from the volume in the tube and the density at  $0^\circ\text{C}$ .

Following the distillation of n-hexane into the reactor and the addition of the required amount of butyllithium, the stirred system was brought up to  $50^\circ\text{C}$  and the butadiene was added so as to maintain a controlled reactor pressure of less than 1000 torr. The extent of reaction was monitored barometrically until a

98-99% conversion was reached. At this time, a 1.0 ml aliquot was withdrawn from the reactor by syringe in order to obtain a GPC molecular weight and to check the extent of reaction to be certain that the butadiene monomer was essentially totally consumed. The reactor was then evacuated and flushed with argon while being cooled to 0°C.  $\text{TiCl}_4$  was then added with vigorous stirring and the reactor was again brought up to temperature (50°C COP 1, 30°C COP 2) and evacuated. The optimum ratio of n-butyl lithium to  $\text{TiCl}_4$  was between 2 to 3 with an overall titanium concentration between  $10^{-2}$  to  $10^{-3}$  moles/liter (18). The addition of  $\text{TiCl}_4$  to the faintly yellow living polybutadienyllithium solution results in a reddish-brown solution containing a dark precipitate.

Propylene gas was then added at a rate sufficient to maintain a reactor pressure of 900 torr. Initial addition of propylene appeared to "solubilize" the catalytic precipitate but after about twenty minutes a noticeable insoluble polymer fraction began to develop. Two hours after the addition of propylene, the pressure was increased to 950 torr and the reactor sealed off. The reactor pressure drop was monitored while polymerization continues. Fifteen hours after the initial addition of propylene, the reaction was terminated by the addition of a 5% solution of HCl in anhydrous, degassed ethanol. The reaction mixture was allowed to stir for one hour under inert conditions. The hexane insoluble precipitate in the reactor was washed several times with ethanol and then dried at 25°C in vacuum. The hexane-soluble products were precipitated into ethanol washed and dried.

Two other polymerizations were carried out for diagnostic purposes. In the first of these, 1,1 diphenylethylene was added in stoichiometric amounts to the n-butyl lithium/hexane mixture in the reactor at 50°C followed by cooling to 0°C and subsequent additions of  $\text{TiCl}_4$  as described above. After reheating the reactor to

50°C, butadiene monomer was added and polymerized to low conversion. The insoluble product (COP 3) was recovered as indicated above and then subjected to exhaustive extractions with methanol. In the second control reaction,  $\text{TiCl}_4$  was added directly to the *n*-butyllithium/hexane mixture at 0°C, stirred, heated to 50°C at which time propylene monomer was admitted to the reactor in the manner described above. The insoluble product (HOM1) was recovered as indicated previously.

The four polymerization reactions are summarized in Table 1.

Table 1 Summary of Polymer Synthesis Procedures

<u>Code</u>	<u>Solvent</u>	<u>Alkylolithium</u>	<u>Monomer 1</u>	<u>Transition Metal</u>	<u>Monomer 2</u>	<u>Products Obtained</u>
COP 1	n-hexane	nBuLi	1,3 butadiene	$\text{TiCl}_4$	propylene	2 fractions: hexane-soluble hexane-insoluble
COP 2	n-hexane	secBuLi	1,3 butadiene	$\text{TiCl}_4$	propylene	2 fractions: hexane-soluble, hexane-insoluble
COP 3	n-hexane	n-BuLi	1,1 diphenyl- ethylene	$\text{TiCl}_4$	1,3 buta- diene	hexane-insoluble
HOM1	n-hexane	n-BuLi	(none)	$\text{TiCl}_4$	propylene	hexane-insoluble

#### Polymer purification

The various reaction products described above were characterized prior to any further purification. Based on IR and NMR experiments the hexane soluble fractions from COP 1 and COP 2 were essentially pure polybutadiene (about 60% *cis* 1,4, 30% *trans*, 1,4, 10% 1,2 microstructure). In both cases GPC molecular weight of this polybutadiene remaining in the reactor was essentially identical to that of the PB sample taken prior to the addition of  $\text{TiCl}_4$ . These molecular weights are

5000( $M_w/M_n = 1.2$ ) and 10,000( $M_w/M_n = 1.2$ ) respectively for COP 1 and COP 2. The weight ratio of soluble to insoluble product in the reactor was 44g/7g and 44g/9g for COP 1 and COP 2 respectively.

The insoluble products of the copolymerization reactions were purified further to separate the block copolymer from unwanted homopolymer species. Extractions were performed with a series of solvents using a constant-temperature extractor similar to that of Russell (22). Extractions with 2-pentanone, hexane, and p-xylene resulted in p-xylene-soluble (80°C) fractions, which will hereafter be referred to as block copolymer. The compositions by weight of these block copolymers were about 40%PB/60%iPP for COP 1 and 60%PB/40%iPP for COP 2. In an attempt to determine whether a significant amount of molecularly-unattached, but crystallized, polypropylene homopolymer was present in the block copolymer, molded specimens of the p-xylene-soluble block copolymers were subjected to electron irradiation under conditions appropriate for crosslinking the polybutadiene while minimizing chain scission of iPP (23). Subsequent extraction with boiling p-xylene resulted in minimal weight losses (a few percent in each case) indicating that the polypropylene contents of the block copolymers are covalently bonded to the polybutadiene moieties.

### Results and Discussion

The molecular nature of the novel PB-iPP block copolymers will be discussed in the context of results of: extensive molecular and morphological characterization experiments, the method of the synthesis employed, and the products obtained from the diagnostic reactions COP 3 and HOM1 (Table I).

Although aluminum alkyls are preferred, lithium alkyls are also capable of forming coordination catalysts. The extension of this scheme to include polymeric

lithium alkyls is in line with the premise of chain-length independence in polymerization reactions and has been demonstrated (24). The further assertion that these systems (living polymeric anion, transition metal salt, monomer) can lead to block copolymers is supported by the observation that the alkylating species remains attached to a coordinatively grown polymer made under Z-N polymerization conditions (25). Thus, in principle, the preparation of a 1,4 polybutadiene-isotactic polypropylene block copolymer by a transformation reaction from an anionic to coordinative mechanism is possible to accomplish.

The underlying basis for this particular transformation reaction was further substantiated by the two model reactions summarized in Table 1. We found that the catalyst system  $n\text{BuLi}/\text{TiCl}_4$  is capable of polymerizing isotactic polypropylene (HOMI). The resultant polypropylene before purification has an isotactic index determined by IR (26), of 70%, a melting point of  $154^\circ\text{C}$ , and a crystallinity of ca 15%, both determined by DSC experiments. Following extraction with hexane and isothermal crystallization from hot *p*-xylene, the same polypropylene showed an isotactic index of 90%, a melting point of  $160^\circ\text{C}$ , and a crystallinity of 30-40%.

In reaction COP 3 1,1 diphenylethylene was added to a solution of  $n\text{BuLi}$  in hexane followed by  $\text{TiCl}_4$  and butadiene monomer. The extent of reaction was kept low and the purified low molecular weight trans 1,4 polybutadiene polymer was shown by high resolution NMR to contain the 1,1 diphenylethylene end group. This result indicates successful coupling of the first and second blocks in our reactions.

In order to contrast the properties of the block copolymers with a known blend of corresponding homopolymers, a series of blends were made by coprecipitation of the purified iPP product HOMI and the soluble polybutadiene from the copolymerization COP 1.

High temperature GPC experiments (140°C in trichlorobenzene, Waters 150C) on blends always revealed two distinct elutions corresponding to the polypropylene, which peaks at an elution volume corresponding to a 250,000 g/mole monodisperse polystyrene, and the polybutadiene, which peaks at a volume corresponding to a 15,000 g/mole monodisperse polystyrene. The polydispersity of the iPP was  $\bar{M}_w/\bar{M}_n = 5$  and for PB it was 2. The block copolymer exhibited a single broad peak,  $\bar{M}_w/\bar{M}_n = 9$ , which was located at an elution volume corresponding to a 300,000 g/mole monodisperse polystyrene. In the absence of a complete understanding of the solution configuration and elution characteristics of a block copolymer of this type, quantitative information on its molecular weight cannot be obtained from the GPC results. However, a clear difference between the block copolymer and the corresponding blend is seen; the block copolymer exhibits a lower elution volume suggesting a higher molecular weight than the corresponding iPP homopolymer in the blend.

Only minor differences between blends and the block copolymers were observed in DSC experiments. Table 2 summarizes the locations of the various thermal transitions in these materials. However, a more detailed study of crystallization kinetics has shown major differences in parameters relating to nucleation, growth, and chain folding in spherulites of the blend and the block copolymers. Preliminary results of this study have already been presented (27) and the full details will appear elsewhere.

Table 2 Thermal behavior of samples as determined from DSC experiments and dynamic mechanical tests (18).

<u>Sample</u>	<u>wt%PB</u>	<u>wt%iPP</u>	<u>TgPB</u>	<u>TgiPP</u>	<u>TmiPP</u>	<u>%Crystallinity</u>
Blend	40	60	-85°C	0°C	153°C	10-15
COP 1	40	60	-75°C to -55°C	3°C	154°C	20-25
COP 2	60	40	-80°C to -70°C	3°C	145°C	10-15
HOM1	0	100	-	-3°C	154°C Before Extraction	20-25
					160°C After Extraction	30-40

In our view the most definitive proof that can be offered to defend the proposed block copolymer structure comes from detailed examinations of the morphologies of these materials. It is now well known that the microphase separated morphologies with dimensions typically on the order of tens of nanometers and the striking uniformity of domain sizes (28) is essentially only achievable in block copolymers. Blends of pure homopolymers exhibit much larger domains typically many micrometers in dimension but which in principle are unbounded at thermodynamic equilibrium; small quantities of block copolymer can have an emulsifying effect in homopolymer blends thereby providing limits on the size of the domains (29).

In view of these morphological concepts, the transmission electron micrographs of Figures 1-3 offer evidence for the block copolymer molecular structures of COP 1 and COP 2. In all micrographs the polybutadiene regions appear darker in contrast owing to the staining action of osmium tetroxide which has been employed

according to conventional methods (30). In Figure 1 a spherical or partially reticular cylindrical morphology is seen very clearly for COP 1. The 0.1 micrometer length scale shown in the figure encompasses many polybutadiene domains which also clearly exhibit a narrow domain size distribution. This morphology was observed very clearly in many parts of the various microtomed sections of COP 1 examined in the electron microscope; in other regions the microdomain structure was still visible but less clear in the micrographs and less regular in form. We believe that Figure 1 is representative of regions of lower iPP crystallinity in COP 1 and the more disrupted microphase-separated morphologies seen elsewhere are representative of regions of higher crystallinity. Figure 2 shows a lamellar morphology for COP 2; again the 0.1 micrometer scale encompasses several lamellae, consistent with block copolymer microphase separation. The fact that the characteristic domain length scale is larger for COP 2 compared to COP 1 is in keeping with the higher PB molecular weight of COP 2. Finally, Figure 3 reveals that COP 1 has the ability to emulsify homopolymer blends of iPP and PB. In this figure we see the morphology of a blend of 45 wt% iPP, 45 wt% PB and 10 wt% COP 1; domains of polybutadiene with characteristic dimensions of about 1 micrometer and smaller are observed. When a similar blend is prepared without the COP 1 in the mixture, complete separation of components occurs resulting in macroscopic layering in the sample preparation container. The results of more detailed studies of the morphologies and properties of block copolymer-emulsified blends of iPP and PB will appear in forthcoming publications.

As a final comment, we note that the efficiencies of our reactions are low, about 10-15% based on the total amount of block copolymer recovered. Only about 35% of the living polybutadienyl lithium survives the transformation reaction, the remainder being terminated at some point in the formation of the Z-N catalyst with



$\text{TiCl}_4$ . Analysis of the ratio of moles of  $\text{TiCl}_4$  per mole of reacted polybutadiene gave numbers in the range of 2 for our polymerizations which is consistent with a previously proposed (31) catalyst composition of  $(\text{RTi}_2\text{Cl}_6 \cdot 3\text{LiCl})$  for reactions of this type.

### Summary

Two high molecular block copolymers of polybutadiene and isotactic polypropylene were obtained in about 15% yield from reactions involving transformation from anionic to Ziegler-Natta polymerization conditions. Various molecular-level characterization methods and certain model reactions support the proposed block copolymer structures, but it was morphological evidence from transmission electron microscopy that provided the most convincing case for the block-like nature of the products.

### Acknowledgements

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#### Figure Captions

- Figure 1 Transmission electron micrograph of an  $\text{OsO}_4$  stained section of COP 1.
- Figure 2 Transmission electron micrograph of COP 2.
- Figure 3 Emulsified morphology of a PB/iPP homopolymer blend containing 10% COP 1.







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